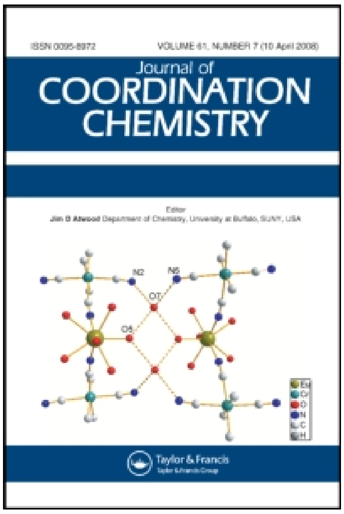

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SOME FACTORS INFLUENCING THE STABILITY OF COMPLEXES WITH LIGANDS CONTAINING NEUTRAL OXYGEN DONOR LIGANDS, INCLUDING CROWN ETHERS

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The formation constants for triethanolamine (L) and ethanolamine (L′) are reported for a variety of metal ions at ionic strength 0.1 molar and 25°. For Cu(II), $\log K_1$ with L is found to be 4.07, while logK values for the equilibria $Cu^{2+} + L + OH^- \rightarrow CuLOH^+$ and $CuLOH^+ + L \rightarrow CuL_2OH^+$ are found to be 12.42 and 1.99 respectively. For Pb(II) with L′, $\log K_1$ is found to be 4.10, while for L $\log K_1$ is 3.39, and $\log K_2$ is 2.47. The equilibria $PbL^{2+} + 2OH^- \rightarrow PbL(OH)_2$ and $2PbL + OH^- \rightarrow Pb_2L_2OH$ are found to have corresponding values of 13.05 and 8.89 respectively. For Ni(II) with L $\log K_1$ is found to be 2.76, and $\log K_2$ 0.84, while $\log K_1$ for Co(II) is found to be 2.25, with $\log K_1$ and $\log K_2$ for Zn(II) 2.05 and 1.23, respectively. The formation constants of ligands containing neutral oxygen donors (alcoholic or ethereal) are examined, and it is concluded that for some metal ions such as Pb(II), Ca(II), or La(III), the inductive effects of the ethylene bridges outweigh the adverse steric effects of increasing the number of chelate rings. For these metal ions, addition of neutral oxygen donors leads to an increase in complex stability, which effect also contributes to the stability of their complexes with crown ethers. For other metal ions, such as Cu(II), Fe(III), or Ni(II), the steric effects outweigh the inductive effects, and the stability of their complexes is not enhanced by neutral oxygen donor atoms.

INTRODUCTION

Neutral oxygen as a donor atom, in the form of alcoholic and ethereal oxygens, is of considerable interest because of the "macrocyclic" effect found in complexes of crown ethers with metal ions such as the alkali and alkaline-earths.[1] In particular, the relatively high stability[2] of these complexes is of interest, as it appears to have no precedent in open-chain ligands. As a first step to an understanding of the complexing properties of crown ethers, we have been examining the stability of complexes with neutral oxygen-donors in open-chain ligands. An interesting effect which emerges is seen in Figure 1. Here we have plotted $\log K_1$ for ODA (oxydiacetate) against $\log K_1$ for the oxalate complexes for all metal ions for which data is available.[3] In passing from oxalate to ODA, we are inserting an ethereal oxygen-donor held in position by two methylene groups. The dotted line in Figure 1 is of unit slope. We see that those metal ions (filled circles) whose complexes increase in stability on inserting the etheral oxygen donor atom into oxalate to give ODA are precisely those metal ions which form stable complexes with crown ethers. On the other hand, those below the dotted line of unit slope are those which do not (open circles).

Why the stability of a complex should increase at all on gaining an extra chelate ring plus an ethereal oxygen donor atom is something of a mystery. The additional stability expected from the chelate effect in passing from a bidentate (oxalate) to terdentate (ODA) ligand will not be found here, since the log 55.5

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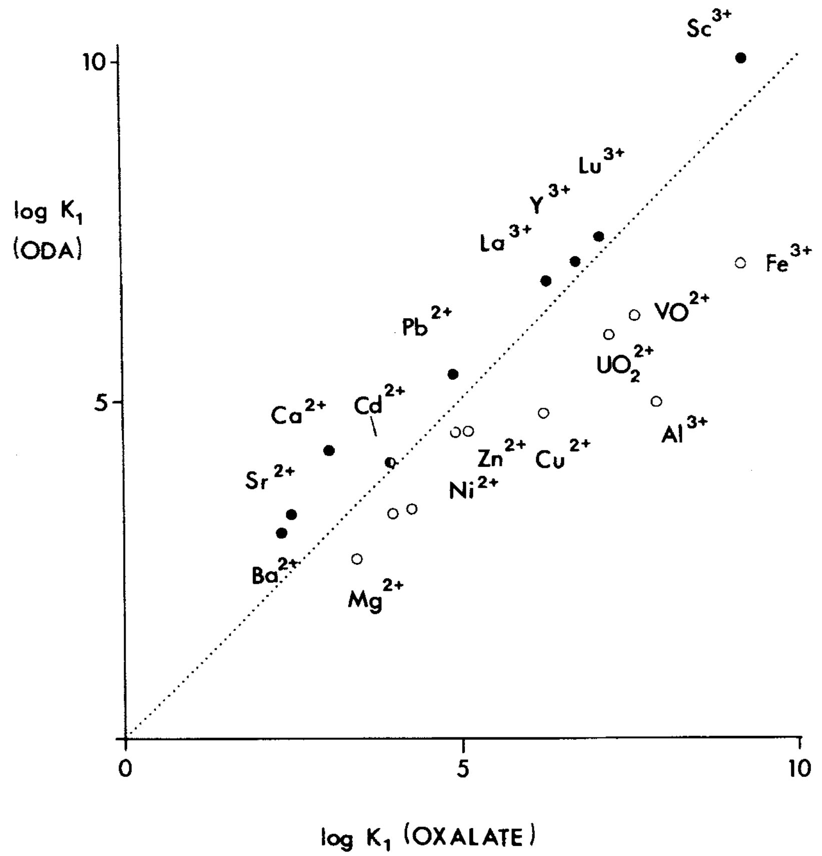

FIGURE 1 Plot of $\log K_1$(ODA) versus $\log K_1$(oxalate) for a variety of metal ions, where ODA is oxydiacetate. All data from reference 3, at ionic strength zero, and 25°. The dotted line is of unit slope, so that metal ions indicated with filled circles above this line show an increase in stability of the ODA complex over that of the oxalate, whereas those below the line (open circles) do not. As discussed in the text, those metal ions which show an increase in stability on adding on ethereal oxygen to oxalate to give ODA are those which show an affinity for crown ethers.

contribution from the asymmetry of the standard reference state will be cancelled out by the fact that unidentate water is present in the standard reference state to the extent of 55.5 M.[4] The extra chelate ring should certainly increase the strain energy of the complex, and we might not at first sight think that the ethereal oxygen should be a significantly stronger donor atom than that in the water molecule replaced upon coordination to the metal ion. However, measurements of gas-phase basicities show that for all metal ions there is a strong increase in complex stability[5] on passing from water to alcohols, and thence to ethers. It thus seems plausible that the increase in stability seen in Fig. 1 is due to greater electron density on the lone pairs of ethers than of water.[6] We have recently[4] completed a study of the complexing properties of ethanolamine, and it appeared that the hydroxyethyl group had little effect on the stability of the complexes formed, as compared with ammonia complexes. We concluded that this was due to a favourable contribution from the inductive effect of the ethylene bridge being cancelled out by the steric strain produced by coordination of the alcoholic oxygen atom. It is apparent from Fig. 1 that Pb(II) is a metal ion for which there is an increase in the stability of the ODA complex as compared with the oxalate complex. It should thus display enhanced stability of the ethanolamine complex if this argument is correct.

As an extension of our earlier work,[4] we report here a formation constant study of triethanolamine with Cu(II), Ni(II), Co(II), Zn(II), and Pb(II), and of the ethanolamine complex of Pb(II). These systems have all been much studied,[7] but in general the results are suspect, because deprotonation of the hydroxyethyl arms to give alkoxide groups was not considered. In most cases the systems have been treated as simple equilibria involving the neutral ligand reacting with the metal ion. Figure 2 is a plot of $\bar{n}$, the average number of ligands which are bound to the metal ion, as a function of triethanolamine concentration. The values of $\bar{n}$ have been calculated assuming no deprotonation of the complex, and their almost total non-superimposability as the ratio of ligand to metal is varied shows that this is, for Cu(II) at least, not a tenable hypothesis. Even where deprotonation of the complex was considered,[8,9] the complexity of the systems, coupled with the simplifying assumptions made, makes it unlikely that the deduced constants are correct. The advent of modern computer programs such as MINIQUAD[10] makes investigation of these more complex equilibria a much less daunting task. In addition, inclusion of all the constants for the hydrolysis of the metal ions themselves in the refinement obviated the problem that take-up of base was due to

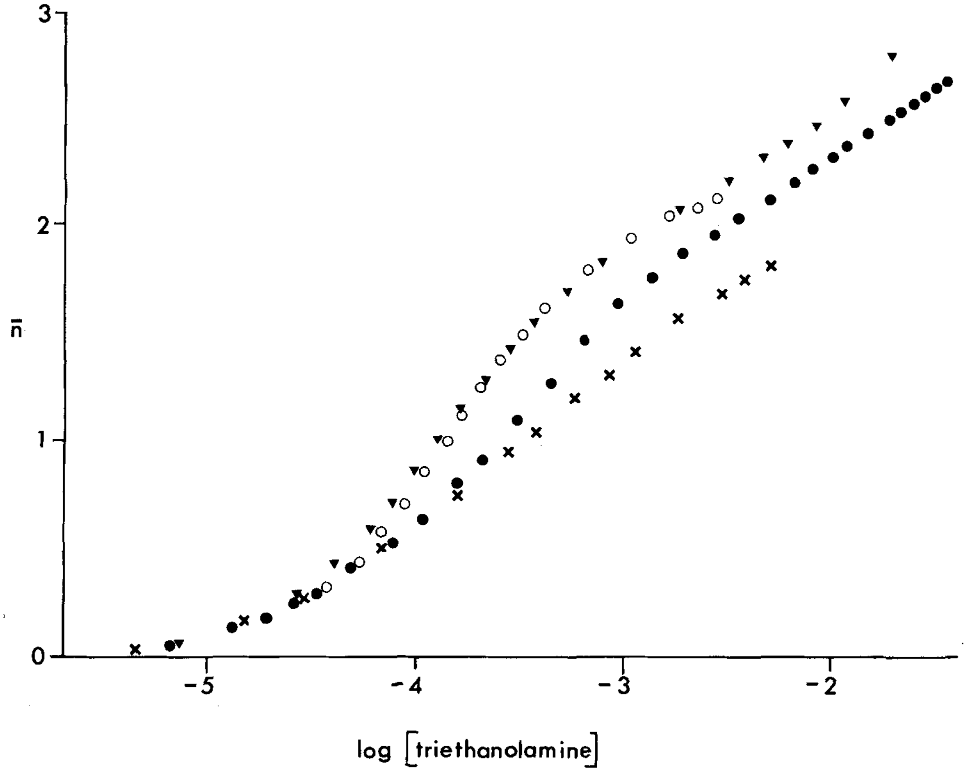

FIGURE 2 Curve of $\bar{n}$ versus log {free triethanolamine} concentration for copper(II). The $\bar{n}$ value is an apparent value calculated assuming that no deprotonated species are present. The non-superimposability of the curves as the ligand to metal ratio is varied shows that this is an untenable hypothesis. Key to titrations: (x), Cu_T = 0.00167M, L_T = 0.09528M; (●), Cu_T = 0.01062M, L_T = 0.06997M; (▲), Cu_T = 0.02439M, L_T = 0.032M; (○), Cu_T = 0.00286, L_T = 0.0139M. Since the actual concentrations varied during the titration, Cu_T is the total copper concentration in the cell at $\bar{n}$ equals 1.0, and L_T the total ligand concentration.

metal ion hydrolysis rather than complex formation, which is a very real possibility with the Pb(II) ion.

EXPERIMENTAL

The metal ions were used as their nitrate salts to make up stock solutions, which were standardized by EDTA titration. Ethanolamine and triethanolamine (both MERCK "Extra Pure") were used to make up stock solutions which were standardized by titration with acid. The ionic strength of the solutions was maintained at 0.1 M using $NaNO_3$, and the protonated ligand nitrate as background salts. The ratios of ligand to metal ion, and the total metal ion concentration, were varied over a wide range in order to ensure that the complexes fitted to the system by MINIQUAD[10] could be regarded with confidence. Measurements of pH were made with RADIOMETER G202B glass electrodes and Ag/AgCl reference electrodes, using a RADIOMETER PHM84 pH meter. The cell was thermostatted to 25.0 ± 0.1°, with N_2 gas bubbled through it to eliminate contamination with CO_2. Titrations were carried out with at least three different metal ion concentrations at different ligand: metal ratios for each metal ion. Data reduction consisted of a "pqr" analysis, whereby a large number of complexes were proposed for the initial analysis, and which were then reduced by the program in successive cycles of refinement to those reported in Table I. Complexes included in the analysis were the ML and ML_2 complexes, plus all possible deprotonated forms of these complexes, plus dimers both deprotonated and non-deprotonated.

RESULTS AND DISCUSSION

The constants determined for Cu(II), Ni(II), Co(II), Zn(II), and Pb(II) with

TABLE I
Formation constants of metal ions with triethanolamine and ethanolamine at 25° and ionic strength 0.1 M.

Metal ion	Equilibrium[a]	LogK	Literature Values[b]	References
Triethanolamine:				
Cu^{2+}	$M + L \rightarrow ML$	4.07 ± 0.03	3.9	12
	$ML + OH \rightarrow MLOH$	8.37 ± 0.01	7.8, 7.63, 7.6	8, 13, 14
	$MLOH + L \rightarrow ML_2OH$	1.99 ± 0.06	—	
	$ML + L \rightarrow ML_2$		2.1	12
Ni^{2+}	$M + L \rightarrow ML$	2.76 ± 0.01	2.27	15
	$ML + L \rightarrow ML_2$	3.6 ± 0.1	3.09	15
Co^{2+}	$M + L \rightarrow ML$	2.25 ± 0.05	1.73	16
Pb^{2+}	$M + L \rightarrow ML$	3.39 ± 0.02		
	$M + 2L \rightarrow ML_2$	5.86 ± 0.04		
	$ML + 2OH \rightarrow ML(OH)_2$	13.05 ± 0.06		
	$2ML + OH \rightarrow M_2L_2OH$	8.89 ± 0.05		
Zn^{2+}	$M + L \rightarrow ML$	2.05 ± 0.01	2.00	16
	$M + 2L \rightarrow ML_2$	3.28 ± 0.01		
Ethanolamine:				
Pb^{2+}	$M + L \rightarrow ML$	4.10 ± 0.05		$B_2 = 7.6$ (?) 17

[a] M = metal ion. L = ligand. OH = hydroxide ion. Charges on species omitted for simplicity. [b] All at ionic strength = 0.5 M, except for ref. 12, which is at 0.1 M.

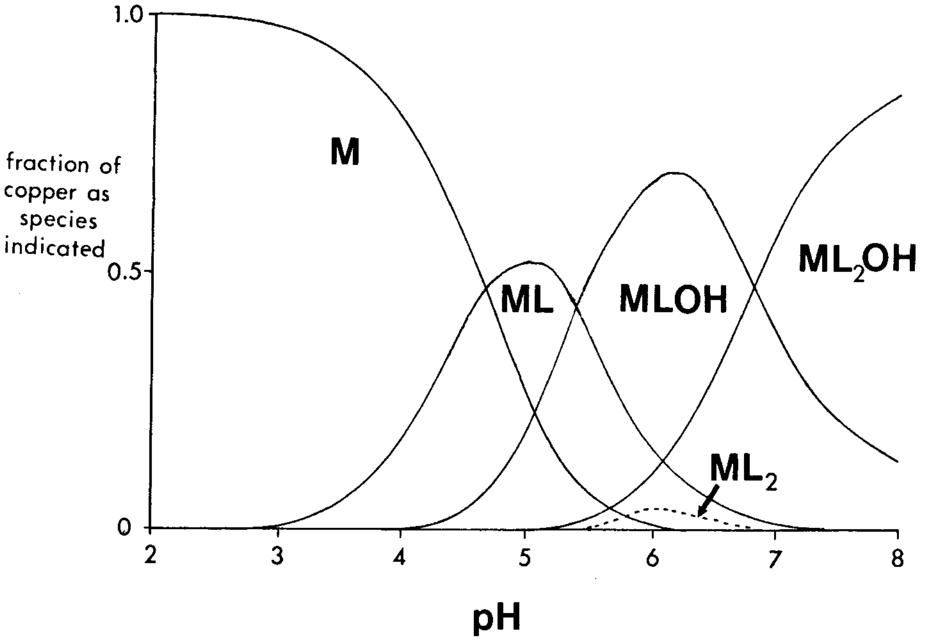

FIGURE 3 Species distribution diagram for triethanolamine (L) with copper(II) (M) as a function of pH. The diagram has been calculated for 0.1M triethanolamine in large excess over the copper(II) ion, which choice minimizes the relative proportions of deprotonated complex species present.

triethanolamine are given in Table I. The Ni(II), Co(II), and Zn(II) systems are simple with no equilibria involving deprotonation of the complex, a finding in agreement with past studies.[7] The equilibria with the Cu(II) and Pb(II) systems with triethanolamine involve deprotonation of the complexes. In Figure 3 is seen the species distribution diagram for Cu(II) with triethanolamine as a function of pH. The calculations were carried out for 0.1 M triethanolamine, in large excess with respect to Cu(II). This optimizes the concentration of complexes with the neutral ligand, over deprotonated complexes. Inspection of Table I shows that a value of $\log K_2$ for Cu(II) with triethanolamine of 2.0 represents a reasonable estimate. Inclusion of this species shows that the CuLOH species is dominant, with the CuL_2 species present to a maximum value of some 4%. Where lower ligand: metal ratios were used, even less CuL_2 would be present, so that reports of this species can be discounted. The reason for this is that the CuLOH species begins (Figure 3) to form at a lower pH than the CuL_2.

What is of particular interest is that, as was found for ethanolamine, $\log K_1$ for triethanolamine for all the metal ions in Table II, is about the same as for $\log K_1(NH_3)$, except for Pb(II), where it is much higher. This suggests that the hydroxyethyl groups of triethanolamine, and of ethanolamine itself, lead to a stabilization of the Pb(II) complex, whereas in the complexes of the other metal ions no such stabilisation is present. This can be readily understood by reference to Figure 1. Pb(II) is one of the metal ions which shows an increase in complex stability with neutral oxygen donors. The interpretation here is that for all the metal ions concerned, the inductive effect should lead to an increase in complex stability, in the absence of steric effects. For those metals above the dotted line, such as Pb(II), La(III), or Ca(II), the increase in steric strain is not sufficient to counter the inductive effect, while for those below the line (*e.g.* Cu(II), Fe(II)) it is.

TABLE II

Comparison of $\log K_1$ values for ammonia, ethanolamine, and triethanolamine at 25° and ionic strength 0.1M.

Metal ion	$\log K_1(NH_3)^a$	$\log K_1$(ethanolamine)[b]	$\log K_1$(triethanolamine)[c]
Cu^{2+}	4.10	4.50	4.07
Ni^{2+}	2.70	3.05	2.76
Co^{2+}	2.10	2.20	2.25
Zn^{2+}	2.18	2.41	2.05
Cd^{2+}	2.65	2.77	2.70
Pb^{2+}	1.6	4.10	3.39

[a] From R.M. Smith and A.E. Martell, "Critical Stability Constants", Vol. 4, "Inorganic Ligands", Plenum Press, New York, 1976, except for Pb^{2+}, which is an estimate from R.D. Hancock and F. Marsicano, *J. Chem. Soc., Dalton Trans.*, 1096 (1976). [b] Reference 4, except for Cd^{2+}, reference 7, and Pb^{2+}, this work. [c] This work, except for Cd^{2+}, reference 7.

Figure 1 is thus of importance in understanding the high stability of the ethanolamine complexes of Pb(II). It also accounts for the high stability of complexes of the ligand tetrahydroxyethylcyclam with metal ions such as Pb(II) and La(III),[11] where the hydroxyethyl "arms" of the macrocycle lead to considerable stabilization. This latter result leads one to speculate that there might be a previously unsuspected chemistry of lanthanides with ligands such as triethanolamine, which possibility we are at present investigating. Finally, it is evident that investigations of ligands with neutral oxygen donors can lead to a greater understanding of the macrocyclic effect in oxygen-donor macrocycles.

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